THE USE OF FLY ASH FOR THE STABILIZATION OF HEAVY METALS DERIVED FROM SEWAGE SLUDGE

By

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CHAPTER I

INTRODUCTION

The land disposal of sewage sludge from a sewage treatment plant in north Tulsa, Oklahoma has created environmentally hazardous levels of heavy metals in the upper horizon of a soil profile. A DTPA extract and subsequent ICAP analysis revealed concentrations of available zinc, copper and nickel to be 348ppm, 104ppm and 33.9ppm respectively. In-situ stabilization of the site is desired. Increasing the soil pH to 6.5 or above has historically been effective to limit mobility and toxicity of heavy metals. Upper and lower horizons were extracted for a pilot greenhouse study, since permission to conduct on-site investigations was denied. The pH of the sludged-soil was 6.4. Using fly ash as a liming material, the pH was adjusted to 6.8 and 7.0. Plant uptake movement was investigated for copper, nickel and zinc for the pH ranges of 6.4 (check), 6.8, 7.0, and recommendations for use of fly ash as a stabilizing agent, based upon the experimental results, are discussed.

CHAPTER II

LITERATURE REVIEW

Sewage Sludge

Sewage sludge is obtained from the processing of waste waters from domestic and/or industrial areas (Mc Calla et al., 1977). Primary treatment removes the solids by gravity settling. Secondary treatment usually is the chemical or biological processes that attempts to remove dissolved or colloidal material. The solids (sewage sludge) removed by these processes are usually high in organic matter and are biologically unstable. The chemical composition of sewage sludge is dependent on numerous factors, including the type of digestion performed, the extent and nature of industrialization in the sanitary district, and the seasonal variability of sewage entering the treatment facility (Sommers et al., 1976).

Land Application of Sewage Sludge

The land application of sewage sludge is initially an attractive disposal method due to the plant nutrients associated with sewage sludge and economic advantages when compared to other disposal methods. However, studies which have examined the use of sewage sludge as fertilizer

discovered several problems and a 1975 CAST study investigating the utilization of sewage sludge for food and fiber production revealed many limitations. A summary of the limitations include the following:

1. Sewage sludges, as a source of plant nutrients, are bulky, low grade fertilizers of variable composition with only 10-20% of the nutrient content of commercial fertilizers.

2. As a low grade fertilizer, transportation of these materials over great distances is not economically feasible.

3. Sewage sludge presents management difficulties when compared to commercial fertilizers for field crop production.

4. Undesirable leaching of soluble salts, particularly nitrate, to ground waters, may limit the rates of sewage sludge application.

5. Sewage sludges contain heavy metals that can accumulate in soils to noxious or toxic concentrations for some plants and are potentially hazardous to consuming animals.

Heavy Metals in Sewage Sludge

The introduction of heavy metals via the sewage sludge is a primary concern. "Heavy metals are 'ubiquitous' in soils, but concentrations indigenous to cropland soils do not appear to be harmful to plant growth" (Chang et al., 1984). Boron, cadmium, cobalt, chromium, copper, mercury, nickel, lead, and zinc are heavy metals commonly found in sewage sludges that are potentially hazardous to plants and animals in the food chain (Chaney, 1973).

Variability of Sewage Sludge

The number and concentrations of heavy metal elements found in sewage sludge depends upon the urban and industrial discharge in the treatment region and the type of secondary treatment employed. Table I describes the variability of Zinc, Copper and Nickel concentrations from sewage sludge samples extracted from eight Indiana cities(Sommers, et al., 1976).

TABLE I

VARIABILITY OF Zn, Cu AND Ni CONCENTRATIONS

	---------Mean PPM----------		
City	Zn	Cu	Ni
Anderson	4442	6079	3184
Crawfordsvillle	14673	8381	1015
Kokomo	20119	2594	649
Lebanon	3787	662	119
Logansport	11454	1747	252
Noblesville	1553	778	81
Peru	2155	871	349
Tipton	11397	1154	80

As Table I indicates, prediction of heavy metal concentration in sewage sludges may be difficult. Once sewage sludges are land applied, there is an initial accumulation of heavy metals in the surface soil. The accumulated metals are subject to four fates: plant uptake, leaching through soil profile, retention on the cation

exchange complex, or precipitation within the soil matrix.

Heavy Metal Movement

The mobility of heavy metals through the soil profile has been widely studied. Lund et al.(1976) discovered that chromium, zinc, and copper migrated 2 meters into the soil profile, while cadmium and nickel traveled 3.5 meters. from a sewage sludge drying bed that had been active for 20 years. Leaching from sewage lagoons was noted when Kirkham (1975) documented movement of 61cm for copper, nickel, zinc, and cadmium in a 3 year period. After application of 136 metric tons of sewage sludge over a four year period, Hinsely et al, 1972, reported elevated levels of Cd, Cr, Cu, Ni, and Zn at 30-45cm depths. Bosewell (1975) reported zinc movement to a depth of 30cm and Cd, Cr, and Cu to 15 cm after sludge application of 168 metric tons/ha in a 2 year study. Hence, the potential for heavy metal leaching must be considered for all areas that have received land application of sewage sludge.

Factors Affecting Heavy Metal Leaching

There are many factors which effect the movement of heavy metals. The chemical form of the metal, the soil CEC, organic matter content, permeability, and pH of the soil are among the most influential. Cunningham et al. (1975) demonstrated the addition of heavy metals as soluble salts were more mobile in soil than heavy metals released from

decomposing sludges. The soil pH has been identified as one of the most significant factors affecting the long-term stability or mobility of heavy metals in soils. Generally, acidic conditions increase solubility and, therefore, increase the mobility of heavy metals. Trefry and Metz (1984) found an increased dissolution of trace metals when the pH of the leaching solution was lowered from 6.0 to 2.2.

Plant Uptake of Heavy Metals

The plant uptake of sludge derived heavy metals has been widely studied. Logan and Chaney (1983) examined the introduction of the heavy metals Cd, Cr and Hg into the food chain from plant materials grown in sewage sludge amended soils. CAST (1980) concluded that forages grown after sewage sludge applications with high concentrations of heavy metals have increased contents of heavy metals, especially cadmium and zinc. Metals have been found to accumulate in target organs in animals fed on sludge grown plants (Furr et al., 1976; Hinesly et al., 1976; Chaney et al., 1978; Williams et al., 1978). Although plants and animals accumulate trace metals after sludge application with no apparent short term toxic effects (Furr et al., 1976; Anderson et al., 1982), the degree to which these metals pose hazards to wildlife is not well documented. Accelerated plant uptake of heavy metals can be phytotoxic. However, plant concentrations of heavy metals can be environmentally hazardous before phytotoxic levels are

achieved (CAST, 1976).

Plant Uptake Influences

Soil pH, cation exchange capacity(CEC), and organic matter content are major factors controlling plant availabilities of sludge-derived metals (Chaney, 1973). However, the uptake of heavy metals by indigenous plants can be minimized by the control of soil pH.

pH and Plant Uptake

There are many studies that examine the decrease of plant adsorption of heavy metals with an increasing soil pH. Valderes et al. (1983) stated plant uptake of nickel and zinc was significantly greater in acid soils in comparison with basic soils, but the differences for cadmium and copper uptake were smaller for the pH range studied. A CAST (1976) reported that, a near ten-fold reduction in Zn, Cd, and Mn content may be achieved by liming acid soils (pH 4.5-5.9) to nearly neutral conditions (pH 6-7). An increase of the concentration of elements in an acidic soil solution is observed, due to the desorption of cations, dissolution of solids and decomposition of organo-mineral complexes (Cottenie, et al., 1983). Furthermore, at an alkaline pH, heavy metal cations become less soluble, due to the formation of carbonate and hydroxide precipitates (Lindsay and Norvell, 1978).

Fly Ash

Fly ash is the fine powder residue that is removed from the flue gases of coal fired electrical plants by mechanical collectors and electrostatic precipators. The physical and chemical characteristics of fly ash vary due to differences in coal types and incineration-collection devices. Generally, fly ash consists of iron and aluminum silicates with lesser quantities of calcium, magnesium, potassium, sodium and sulfur oxides and a carbon content of less than five percent (Chang et al., 1977). Fly ash from most power plants has a suspension pH range of 6.5-10.5 and has sufficiently high neutralizing capacity for use as a liming material (Doran and Martens, 1972). The ability of fly ash to provide trace elements is well documented. Phung et al., 1979 acknowledge that fly ash had higher concentrations of B, Co, Cr, Cd, Mo, Ni, Pb, As and Se than would normally be found in soils. Furr et al., 1978, determined various concentrations of 41 elements in fly ash, and found increased levels of arsenic, boron, magnesium and selenium in crops grown on fly ash amended soils.

Traditional sinks for fly ash have involved the use of fly ash in construction materials, primarily Portland cement, or disposal of fly ash in landfills near the generation site. The current EPA regulations require the retired disposal areas to be covered with topsoil and a permanent vegetative cover established. The creation of a fly ash-soil admixture with up to twenty percent fly ash for

the production of Bermudagrass appears successful (Foreman, 1988 unpublished data; Morrill 1990 PSO project summary).

CHAPTER III

MATERIAL AND METHODS

Soil

Sludge treated land was sampled and two sections the soil profile soil were removed for testing: surface and subsurface. Sludge had been incorporated into the surface horizon, while the subsurface was free of sludge incorporation. The soil is classified as a Coweta-Bates complex (USDA). The Coweta soil series is characterized as loamy, siliceous, thermic, shallow, Typic Hapludoll, whereas the Bates soil series is classified as a Fine-loamy, siliceous, thermic Typic Arigiudoll. Table II (Radtke, 1990) details onsite and background (off-site) soil characteristics.

Columns

Thirty-six PVC columns were designed for profile reconstruction. The PVC pipe used for columns was 10.16cm in diameter and was cut into 38cm lengths. Perforated caps, to allow for drainage, were glued to the bottom of each 38cm length. Glass wool was placed at the bottom of the column to prevent soil from exiting through the cap perforations.

TABLE II

MEASURED PROPERTIES OF CONTAMINATED AND BACKGROUND SOIL USED FOR STUDY

	Contaminated Soil		Background Soil	
	Topsoil	Subsoil	Topsoil	Subsoil
pH	6.6	6.1	5.8	5.5
CEC(Cmol/kg)	30.89	21.25	21.05	22.29
% O.C.	4.1	0.7	1.5	0.7
Texture	L	CL	CL	CL
NO_3 (kg/ha)	168	20	-	-
P (kg/ha)	313	170	-	-
K (kg/ha)	386	511	-	-

The columns were placed in a wood frame to maintain vertical position. The wood frame contained a sliding leachate collection tray at the base.

Plants

Three forage crops, Alfalfa, Medicago sativa L., var. Ok-68; Tall fescue, Festuca arundinacea Schreb.; and Sudangrass, Sorghum bicolor L. were selected for study due to their interstitial competitive characteristics and commonness. The individual column planting rates related to field planting rates of 34 kg/ha (0.028g/81cm^2), 16 Kg/ha (0.013g/81cm^2), and 20Kg/ha (0.016g/81cm^2) for Alfalfa, Tall fescue and Sudangrass respectively. The seeds were planted

at a depth of 0.5cm uniformly distributed in the column surface.

Fly Ash

The fly ash used for pH amendment was obtained from the Public Service Company of Oklahoma electrical generating plant at the Oolagah, Oklahoma. The fly ash was derived from Wyoming coal shipped by railroad to the power station. The percent calcium carbonate equivalent of the fly ash was determined to be 47% by neutralization with dilute HCl (Foreman 1988, unpublished data). Table III details the element concentration of fly ash determined by the EPA's Kerr laboratory at Ada, OK by ICAP analysis.

Procedure

Approximately 50Kg of upper and lower soil horizons were extracted from the site. The soil was transported to the laboratory in plastic containers where it was air-dried and ground to < 2mm. Bulk densities of constructed soil columns were 1.37g/cm^3 for the topsoil and 1.41 g/cm^3 for the subsoil portions. The column subsoil portion was prepared by placing 2900g of subsoil into 2059.25cm^3 of column volume(25.40cm deep). The 1.37 g/cm^3 density for the topsoil was created by the addition of 1411g sludge incorporated soil into the remaining 1029.66cm^3 of column volume (12.70cm). The pH of the columns was altered by addition of fly ash. According to the soils buffer index

TABLE III

ELEMENTAL CONTENTS OF FLY ASH

element	percent %	element	mg/kg
Silicon	13.1	Nickel	94
Calcium	28.5	Cobalt	80
Aluminum	12.2	Lead	64
Iron	4.4	Arsenic	<50
Magnesium	4.0	Mercury	<50
Sodium	0.76	Lithium	38
Titanium	0.68	Selenium	28
Strontium	0.42	Silver	20
Potassium	0.25	Molybdenum	20
Barium	0.16	Germanium	<18
Zinc	0.12	Thallium	<17
Boron	0.12	Beryllium	8.7
Vanadium	0.35	Antimony	6.7
Manganese	0.028	Tellurium	<6.0
Copper	0.022	Cadmium	2.6
Chromium	0.011		

and percent effective calcium carbonate equivalent the pH adjustment to 6.8 required 14.8 Mg/ha (12.00g/81cm^2) of fly ash. The adjustment of pH to 7.0 required 19.1 Mg/ha (16.0g/81cm^2) fly ash. The fly ash and topsoil were homogeneously mixed to ensure rapid pH adjustment and experimental plants seeded immediately after mixing. The columns were separated into three groups according to crop species. The crop species were subdivided according to ash treatment levels, zero ash, ash treatment to pH 6.8, ash treatment to pH of 7.0, for a total of nine columns. The experiment was replicated four times, totaling thirty-six columns. The treatment columns were placed into the wood

frame in a random order within replications.

Fertilization was not required as analyses (Table II) indicated levels of nitrogen, phosphorus and potassium were adequate. Upon plant emergence, columns were irrigated with 100mL tap water every other day. Forage samples were taken after the first month of growth, and at three week intervals thereafter for a total of seven harvests. The forage was removed flush with the top of the column and placed in paper bags for oven drying. The forage samples were dried, ground, and digested with nitro-perachloric using a digestion block. The digested material was analyzed for copper, zinc and nickel with a Perkin-Elmer 3030b Atomic Adsorption Spectrophotometer. Plant zinc was measured at wavelength 213.9nm and slit width of 0.7nm. Determination of plant copper was accomplished using a wavelength of 324.8nm and slit width of 0.7nm. Finally, plant concentration of nickel was evaluated using the 232nm wavelength and a 0.2nm slit width.

At the conclusion of the growth phase of the experiment soil samples were taken by splitting the columns and sampling the soil in five zones: 0-2cm (surface), 12cm (bottom of upper horizon), 15cm (upper zone of subsoil), 27cm (middle of lower zone) and at 38cm (base of lower horizon). Available copper, zinc, and nickel were determined by the DTPA extraction procedure (Norvell and Lindsay, 1978; Barbanck and Workman, 1987). The resulting extract was analyzed by a Perkin-Elmer 3030b Atomic

Adsorption Spectrometer. Soil zinc was determined by using the 307.9 nm wavelength and a slit width of 0.7nm. The 324.8nm wavelength with a slit width of 0.7nm option was used to detect copper in the DTPA extract, while the 341.5nm wavelength with a slit width of 0.2nm was used to determine soil nickel. The resulting data was evaluated with the use of SAS software.

CHAPTER IV

RESULTS AND DISCUSSION

The analyzed data revealed several soil-plant interactions involving the use of fly ash to increase soil pH. The results are similar to previous studies which used calcium carbonate as the pH adjusting material (Valdares et al., 1983). The plant and soil results will be discussed in separate sections.

Plant Results

The plant data reveals several pH and metal uptake interactions. The initial examination of the data reveals that an increasing pH, i.e. increased fly ash application, decreased the average plant content of copper, nickel, and zinc for the three forage species examined. This phenomena is illustrated in Figures 1, 2, and 3. Probability coefficients (P) are used to indicate the statistical possibility of an occurrence. Subtracting the probability coefficient from 1 and multiplying by one hundred, gives the percent chance of a given interaction. The data in Figure 1 has a probability coefficient (P) of 0.0001 meaning there is a 99.99% chance of a pH and forage copper content interaction. The Figures illustrate a strong relation

between pH and plant accumulation of copper, nickel and zinc in greater than average concentrations for usual plant materials. Six parts per million of copper, in dry tissue, and 20ppm of zinc is considered adequate (Salisbury and Ross, 1985). The total average copper content for the forage species examined is 13.63 ppm (Figure 1), double the adequate amount. The normal or average concentration of nickel in plant tissue is not known. It has not been proven if nickel is required for plant growth. The average nickel content for the forage crops grown without added ash was 19.33 ppm (Figure 2) and was reduced to 13.46 ppm with the high fly ash treatment to pH 7.0. However, average plant zinc for the crops grown in soils not treated with sewage sludge was to 97.35 ppm (Figure 3).

The pH increase, due to fly ash application, resulted in the reduction of copper, nickel and zinc in the plant materials removed over seven harvest dates.

Of special interest is the difference in metal uptake by the forage crops tested. Fescue, absorbed the highest concentration of copper, nickel and zinc. Alfalfa contained the lowest concentration of nickel and copper, while sorghum contained the lower amounts of zinc. Figures 4, 5, 6 detail the amount of metals absorbed for each crop species examined. The dense fibrous roots of the fescue plant favored the uptake of the heavy metals due to their location in the sludged zone. Alfalfa, a leguminous plant, maintains a taproot system that generally positions roots deeper than

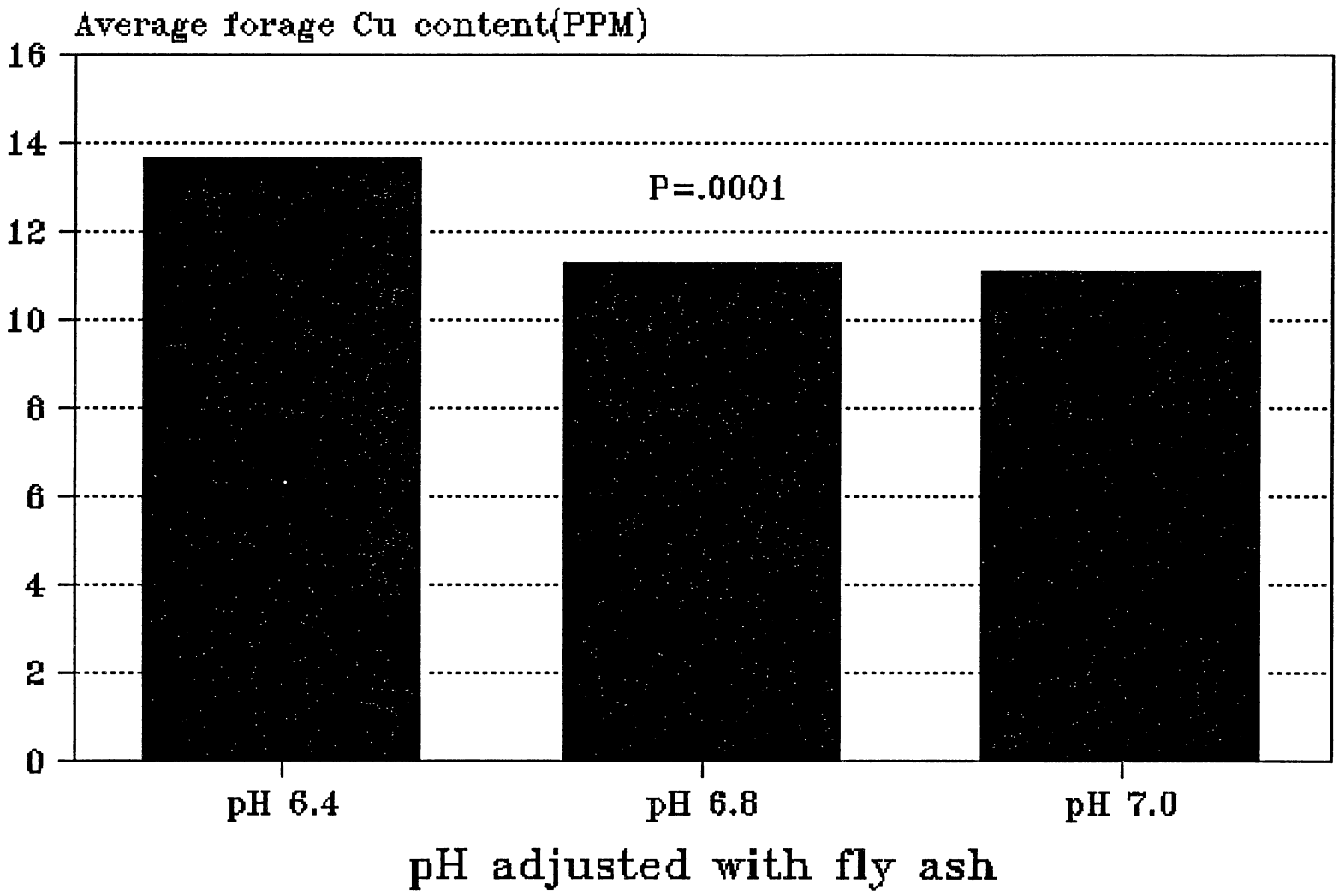

Figure 1. The Forage Average Copper Content in Response to a pH Change Due to the Addition of Fly Ash.

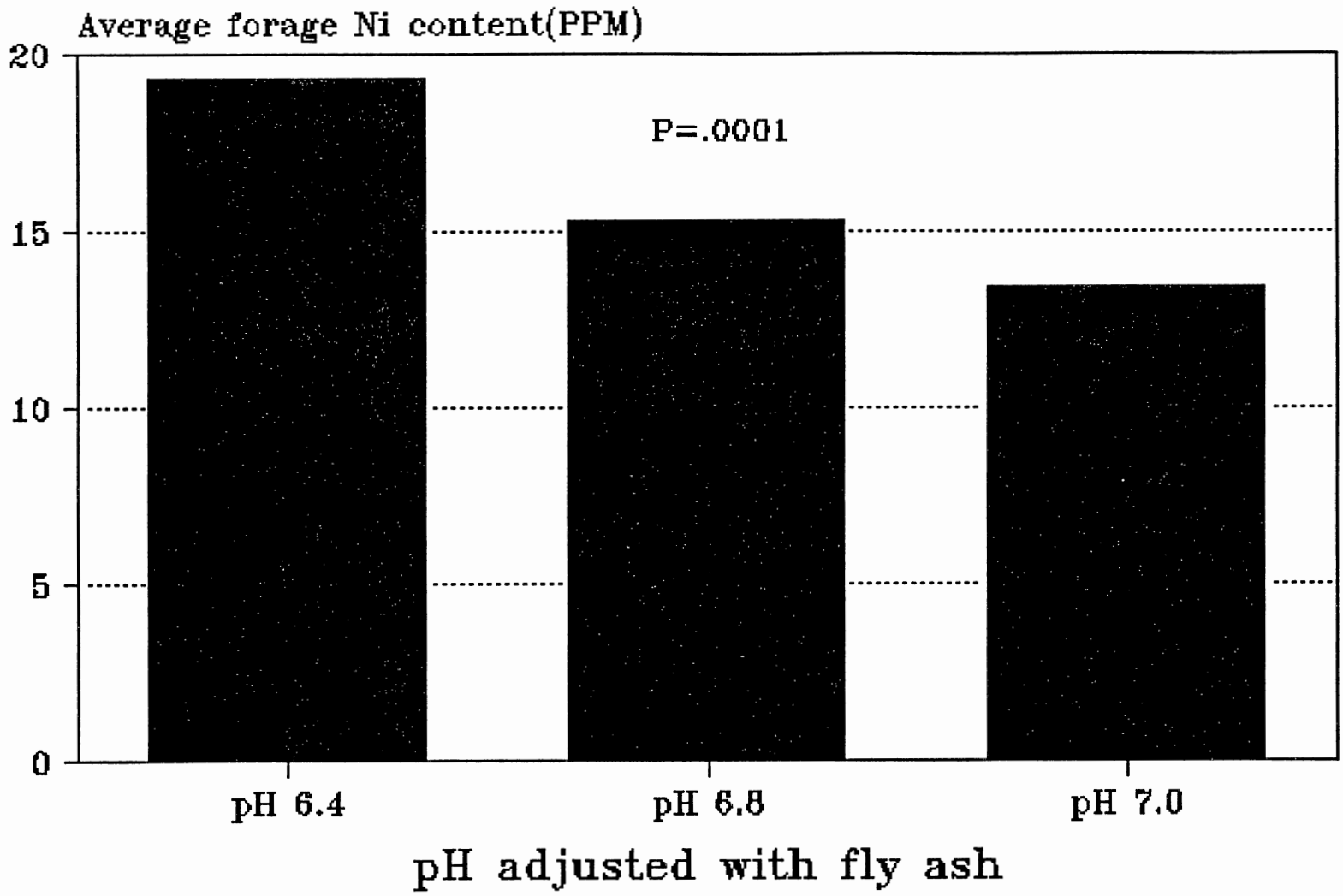

Figure 2. The Forage Average Nickel Content in Response to a pH Change Due to the Addition of Fly Ash.

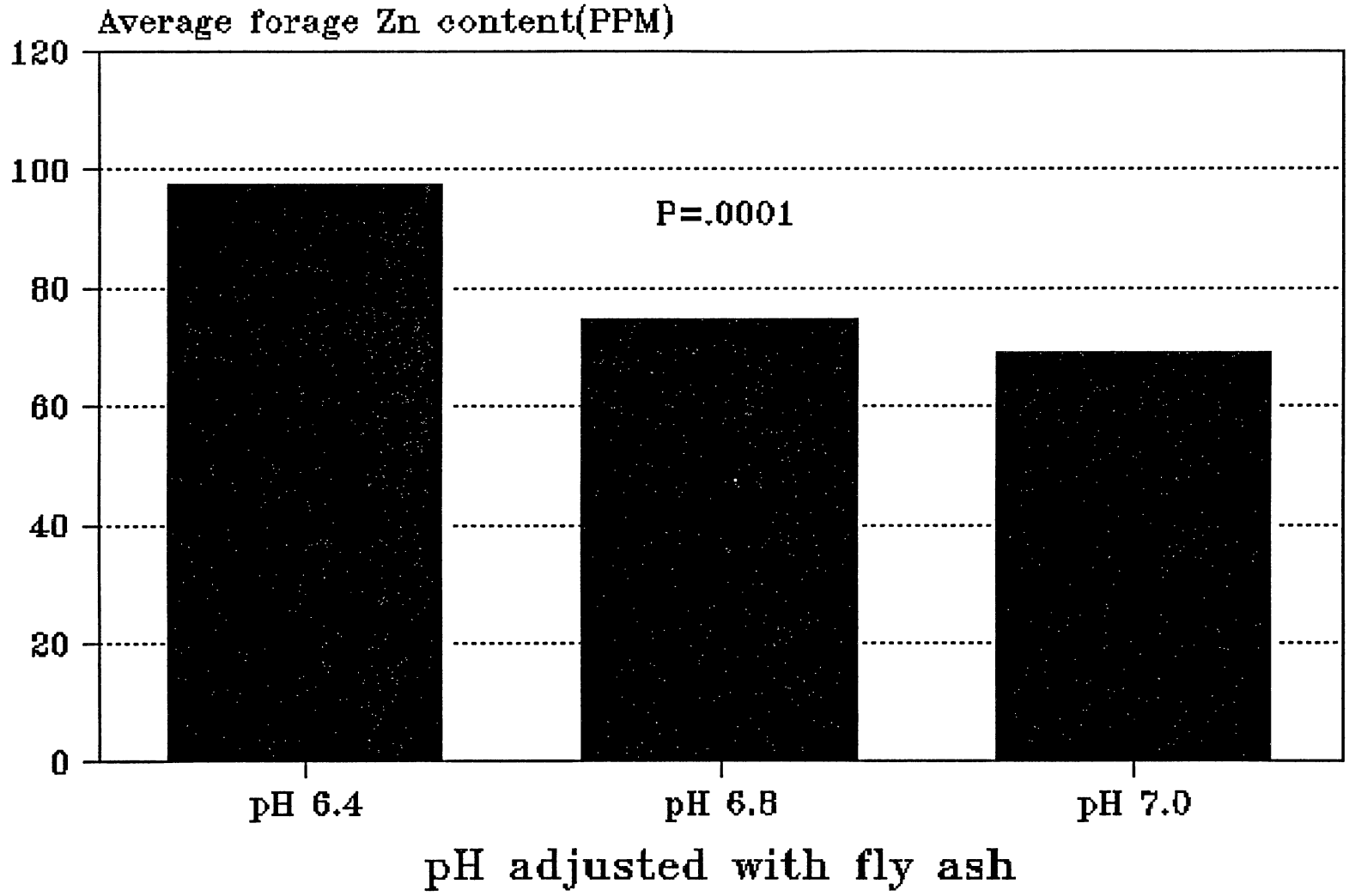

Figure 3. The Forage Average Zinc Content in Response to a pH Change Due to the Addition of Fly Ash.

the fescue and sorghum counterparts. Average metal content for the three forage species is plotted over the pH scale from the points of pH 6.4 to pH 7.0 as illustrated with Figures 7, 8, 9. Although, not regression curves, it represents the trend for decreasing metal uptake with coefficients of 0.0003, 0.0001, and 0.0004 for each element respectively. However, the percent reduction that exists for each crop and element varies.

The dry tissue concentration of copper has the smallest percent reduction due to ash treatment. Increasing the pH to 7.0 reduced the copper uptake 28.49% in fescue when compared to fescue grown in pH 6.4 sludged soils i.e. no fly ash treatment. Sorghum grown in soils amended to pH 7.0 contained 28.15% less copper than sorghum grown in pH 6.4 conditions. The copper dry tissue concentration in alfalfa varied throughout the pH scale. The mean alfalfa copper content was reduced 4.44% by increasing the pH to 6.8 from 6.4. However, at pH 7.0 the copper content increased 10.35% from pH 6.4 and 14.37% from the pH 6.8 treatments.

The concentration of plant nickel was reduced for all forage using fly ash to increase the soil pH ranges. The nickel content in alfalfa was reduced 19.09% by increasing the pH from 6.4 to 7.0. Fescue grown in ash treated soils to pH 7.0 contained 38.83% less nickel than fescue grown in no treatment conditions. Sorghum grown at pH 7.0 maintained nickel concentrations of 30.48% less than the pH 6.4 study. Fescue demonstrated a 41.88% reduction of zinc uptake by

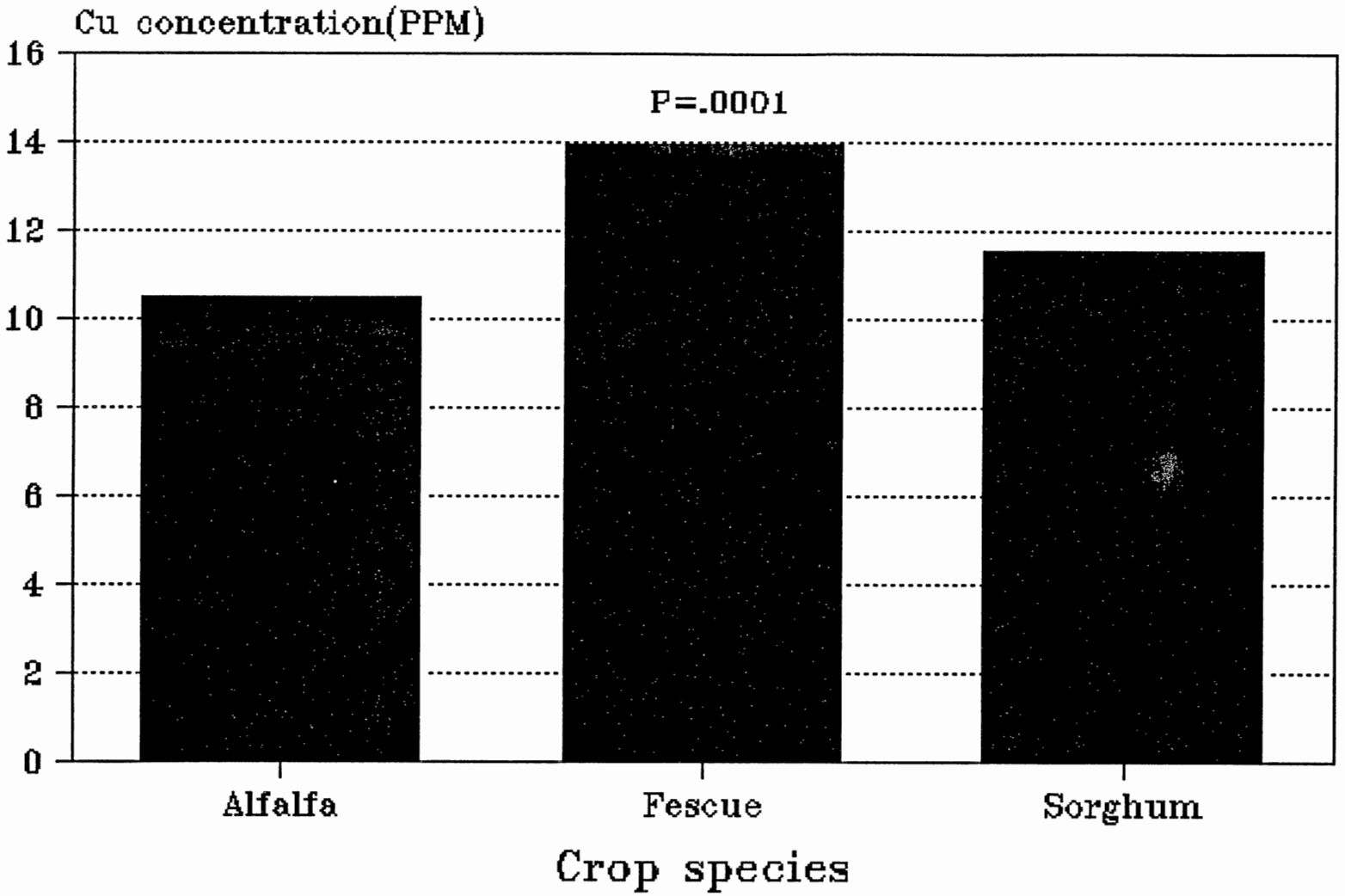

Figure 4. The Average Copper Content for Each Forage Species.

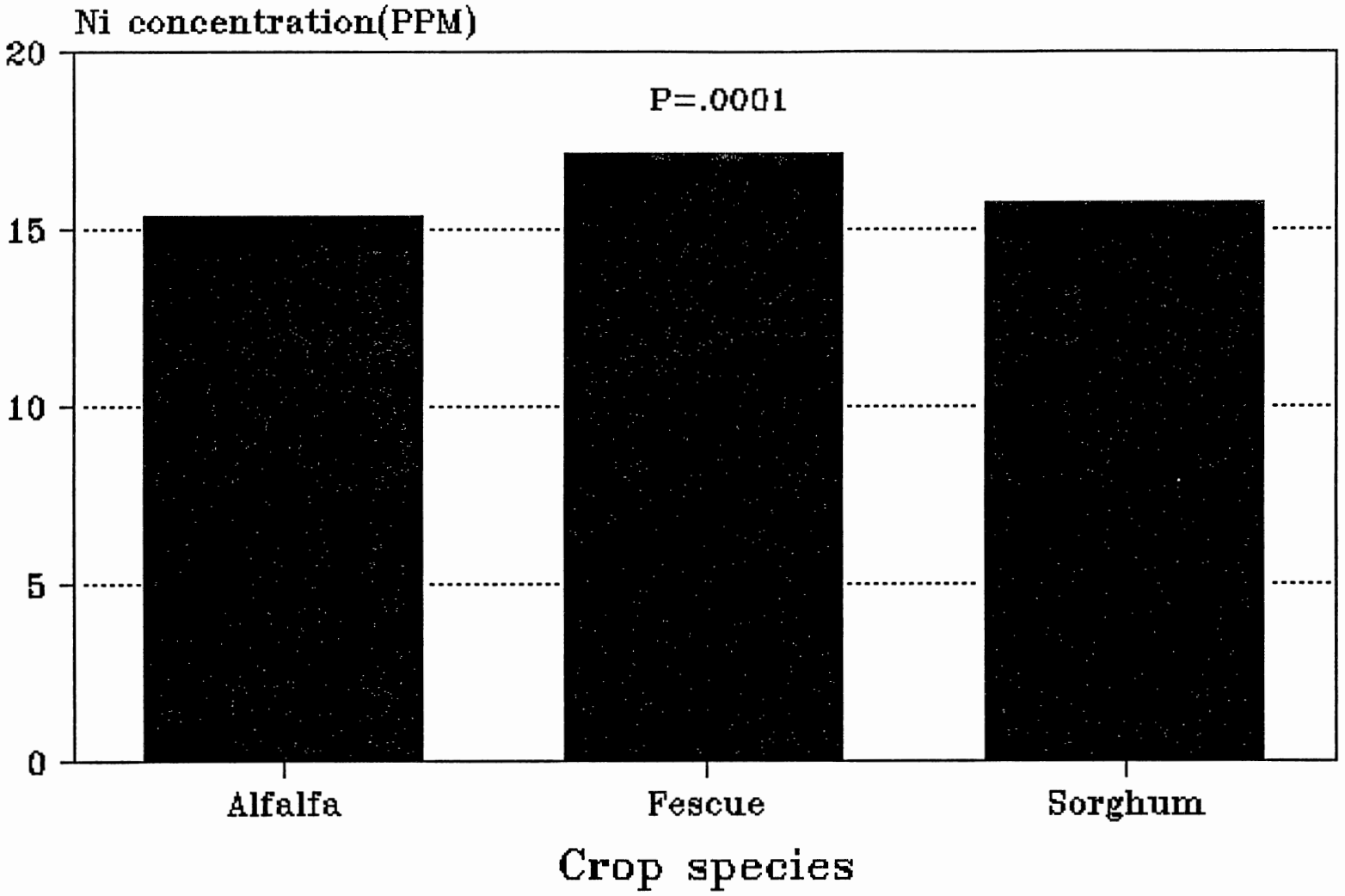

Figure 5. The Average Nickel Content for Each Forage Species.

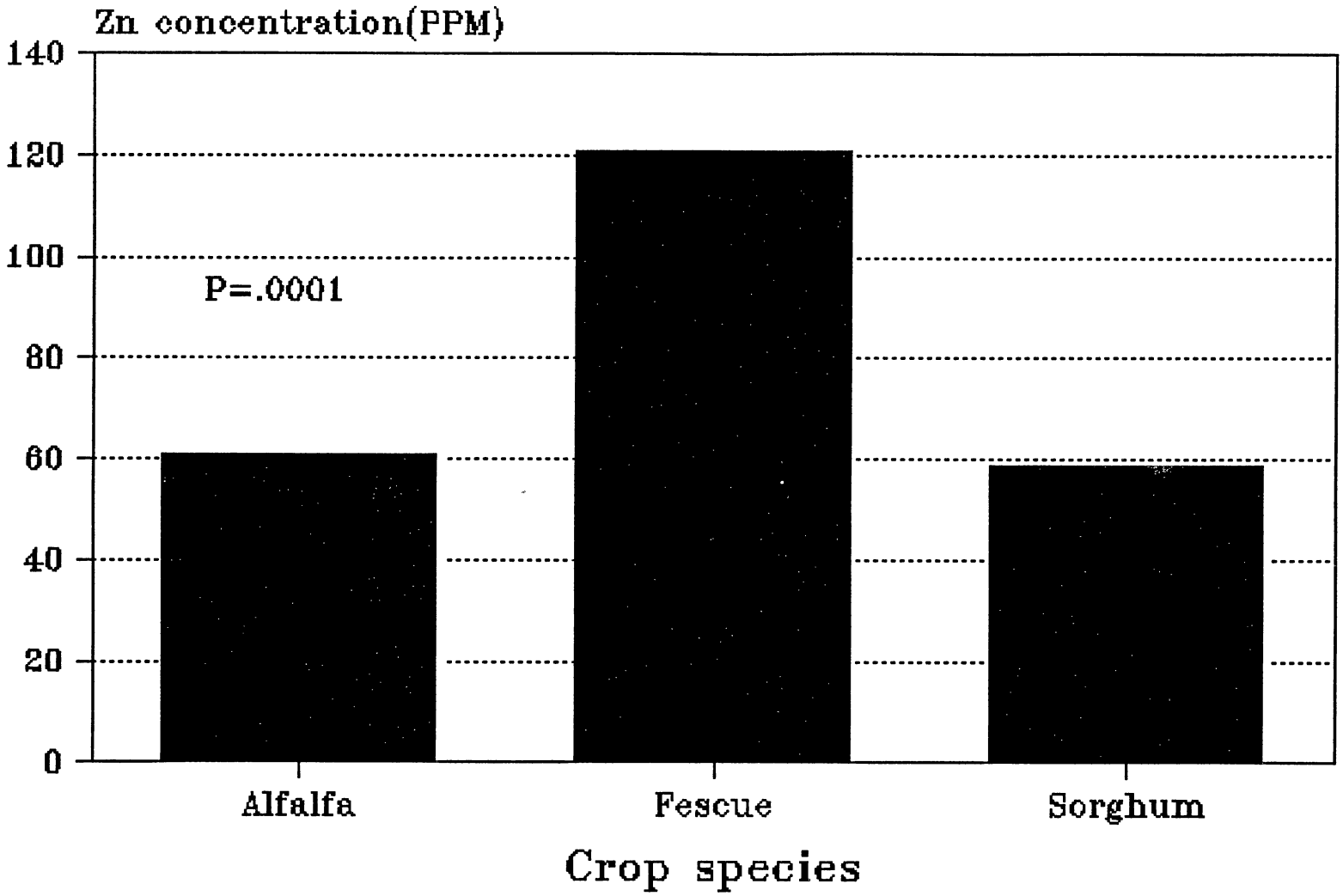

Figure 6. The Average Zinc Content for Each Forage Species.

increasing the pH in the soil columns to 7.0 from 6.4. The zinc content in sorghum decreased 23.43% when fly ash was used to increase the soil pH to 7.0 from 6.4. Again, alfalfa showed the smallest change in metal uptake with increasing pH. The zinc content of alfalfa was reduced 7.49% by increasing the pH to 7.0 from pH 6.4 of the sludge treated soil.

The copper and zinc contents in dry plant tissue were effected at the time of harvest. Nickel maintained a stable level during most of the greenhouse growth experiment. Figures 10, 11 and 12 illustrate the fluxes of metal concentration over the greenhouse experiment time. Figure 10 illustrates the highest levels of copper were at the first clipping for alfalfa and fescue. Sorghum maintained a steady concentration of copper for the first nine weeks and slightly increased for the remaining period. Figure 11 shows nickel concentrations to be highest in sorghum and fescue at the time of the first clipping and leveling off after the first harvest with little fluctuations thereafter. The concentrations of nickel in alfalfa were about 15 ppm for the entire greenhouse experiment. Unlike copper and zinc, nickel concentrations in plant were not statistically linked to harvest date. The probability coefficient for a nickel-crop-harvest date interaction is 0.1739 whereas for copper and zinc it is 0.0014 and 0.0004 respectively.

The use of LSD's were employed to determine the statistical significance of individual cations at various pH

levels. There was a significant difference in the concentration of plant copper from a pH 6.4 and 6.8. However, from pH 6.8 to pH 7.0 there was no significant difference.

The use of LSD's revealed the crops examined to contain significantly different concentrations of plant Nickel at pH 6.4 to pH 6.8 and pH 6.8 to pH 7.0.

Plant Zinc responded similar in statistical nature as plant copper being statistical difference at pH 6.4 to pH 6.8 and showed no difference in plant zinc concentrations at pH 6.8 and pH 7.0.

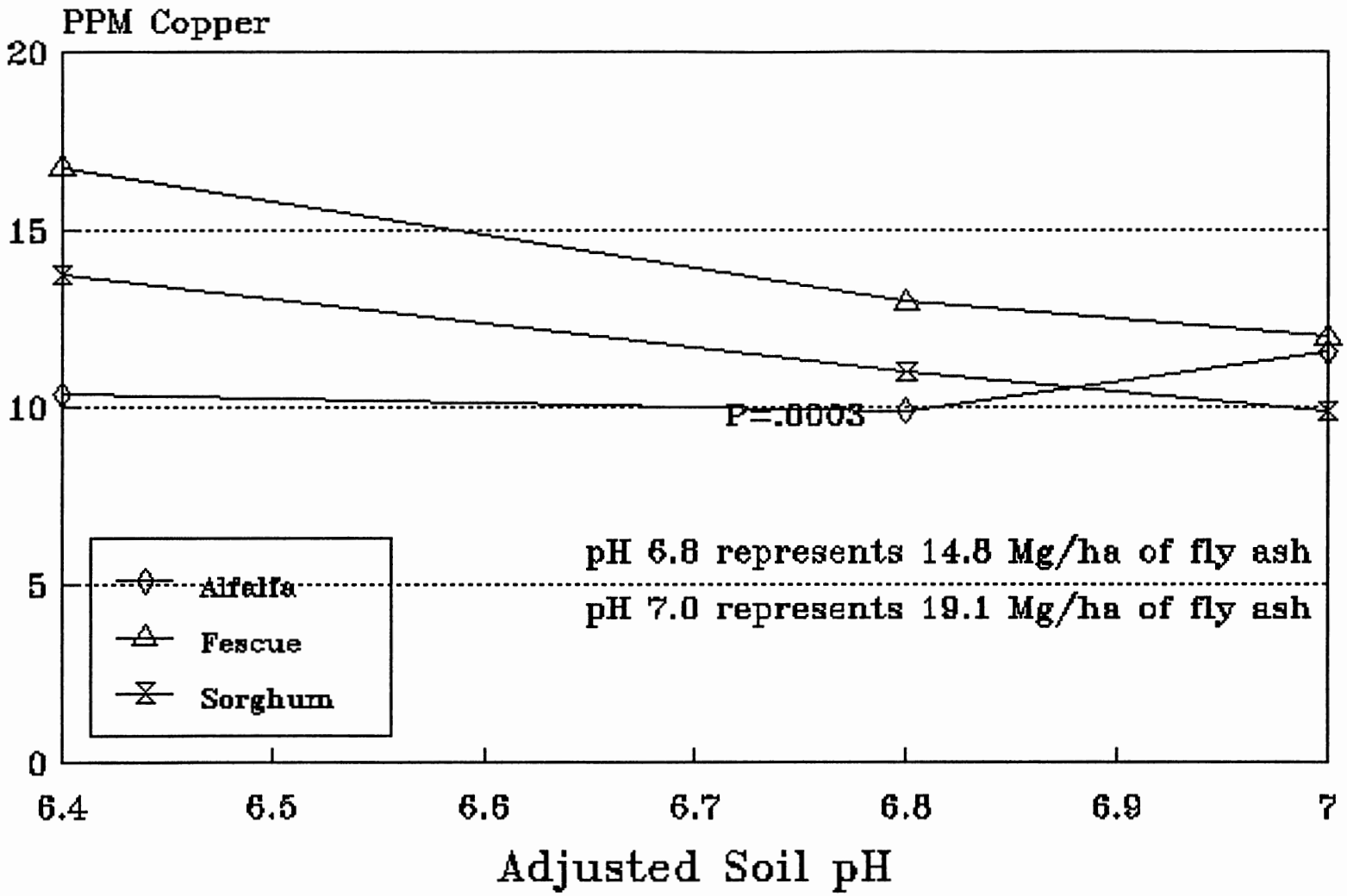

Figure 7. The Reduction of Copper Content in Three Forage Crops with Fly Ash Addition to pH 6.8 and 7.0.

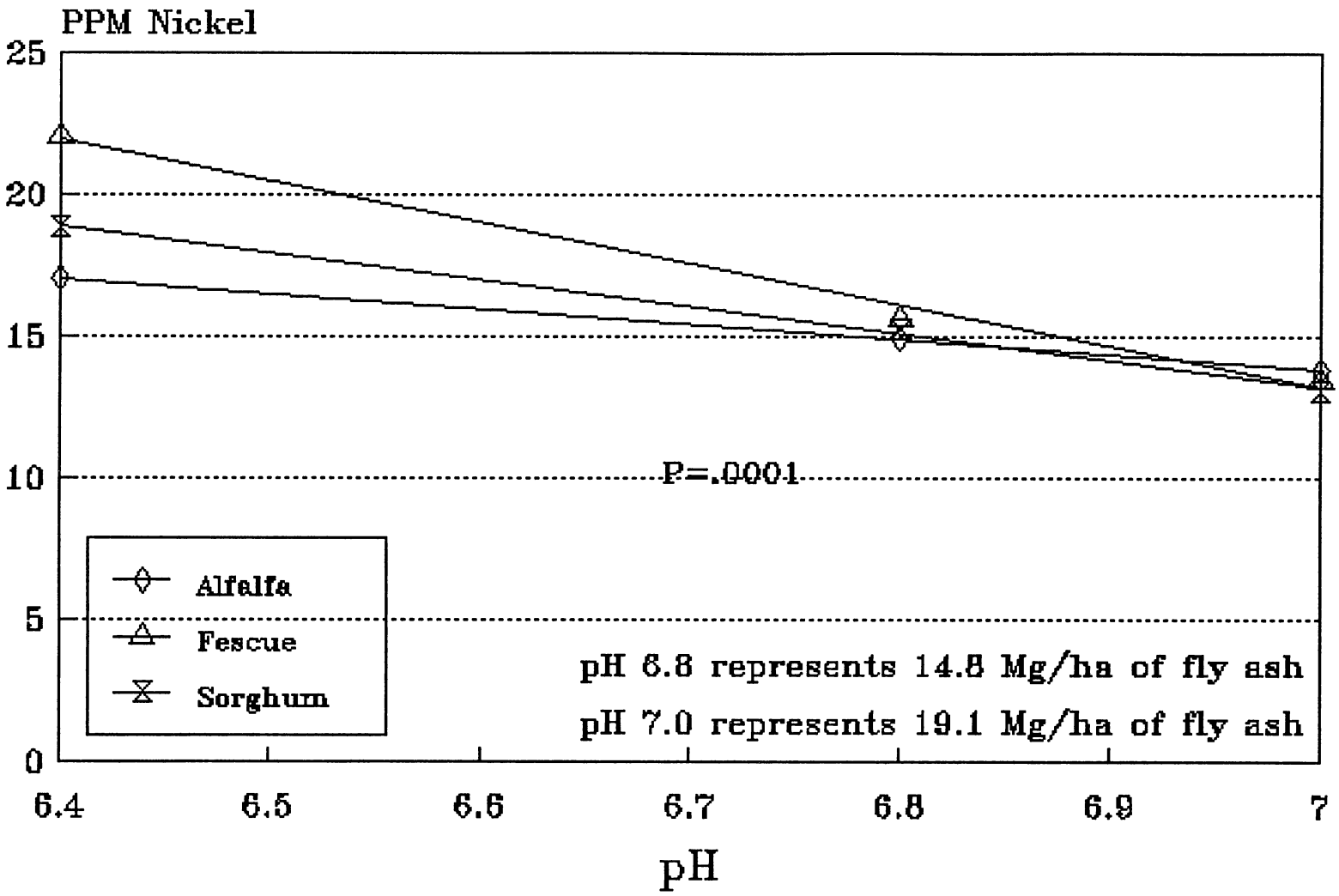

Figure 8. The Reduction of Nickel Content in Three Forage Crops with Fly Ash Addition to pH 6.8 and 7.0.

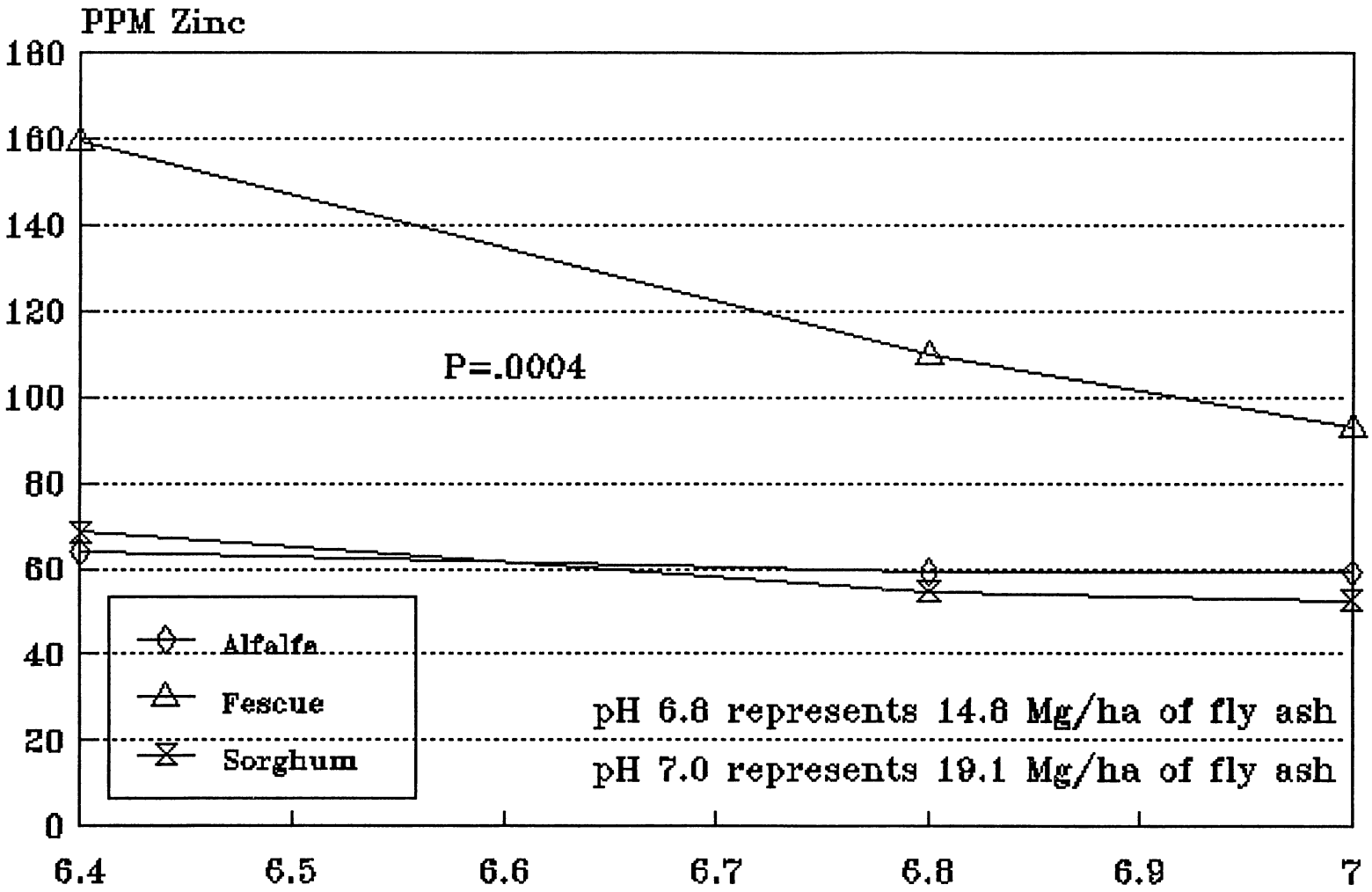

Figure 9. The Reduction of Zinc Content in Three Forage Crops with Fly Ash Addition to pH 6.8 and 7.0.

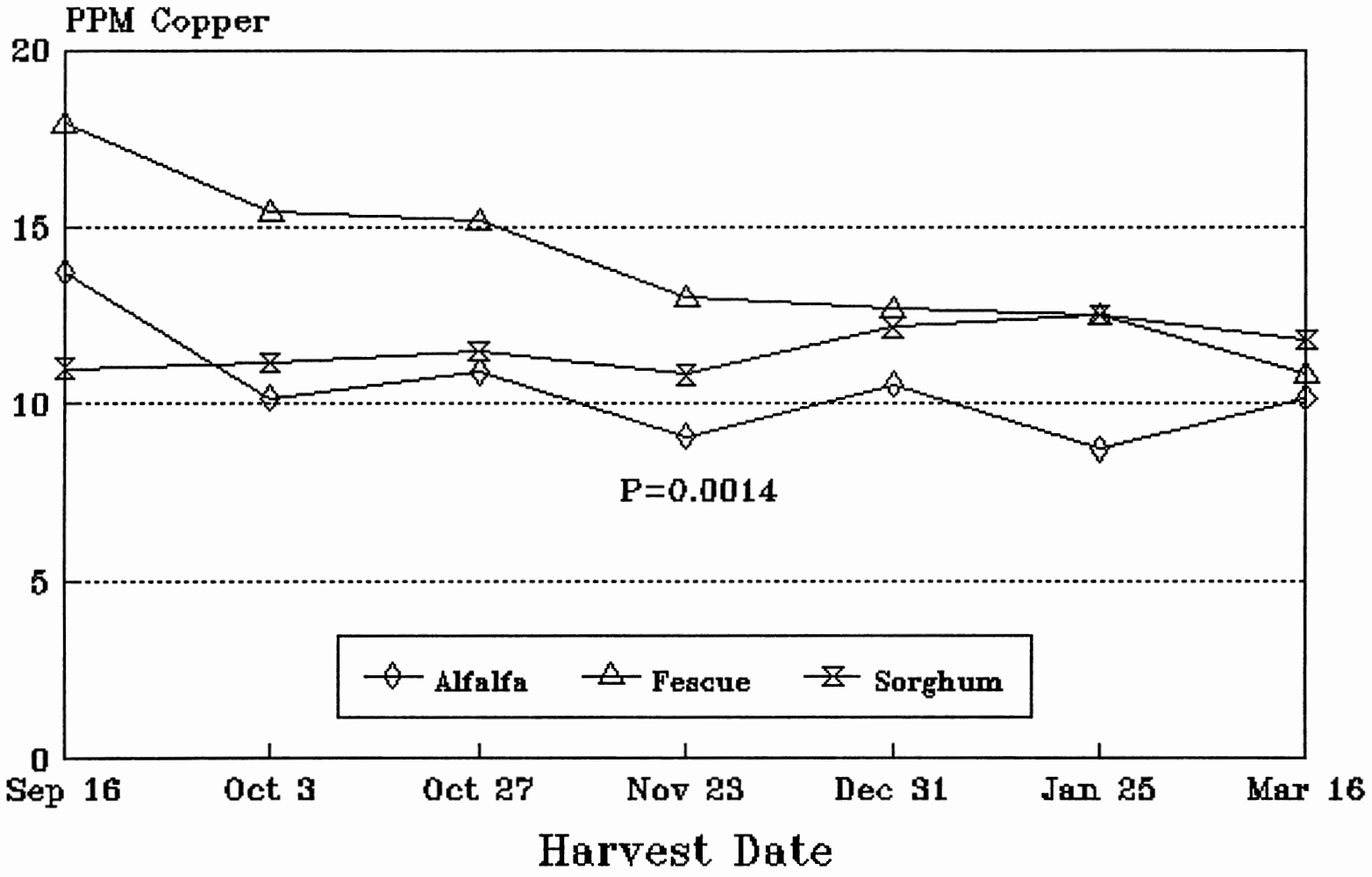

Figure 10. Average Copper Concentration in Forage Crops During Greenhouse Study.

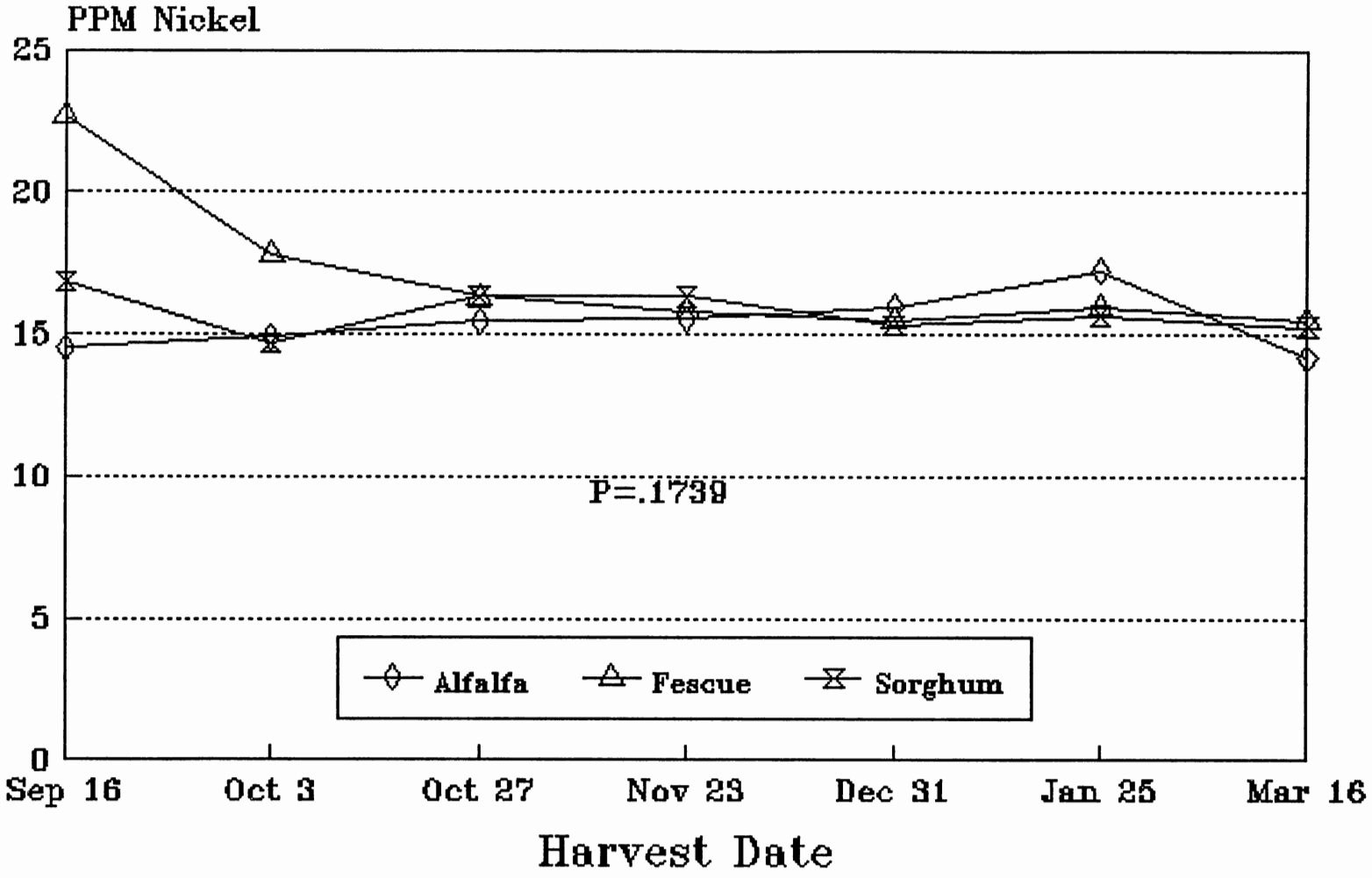

Figure 11. Average Nickel Concentration in Forage Crops During Greenhouse Study.

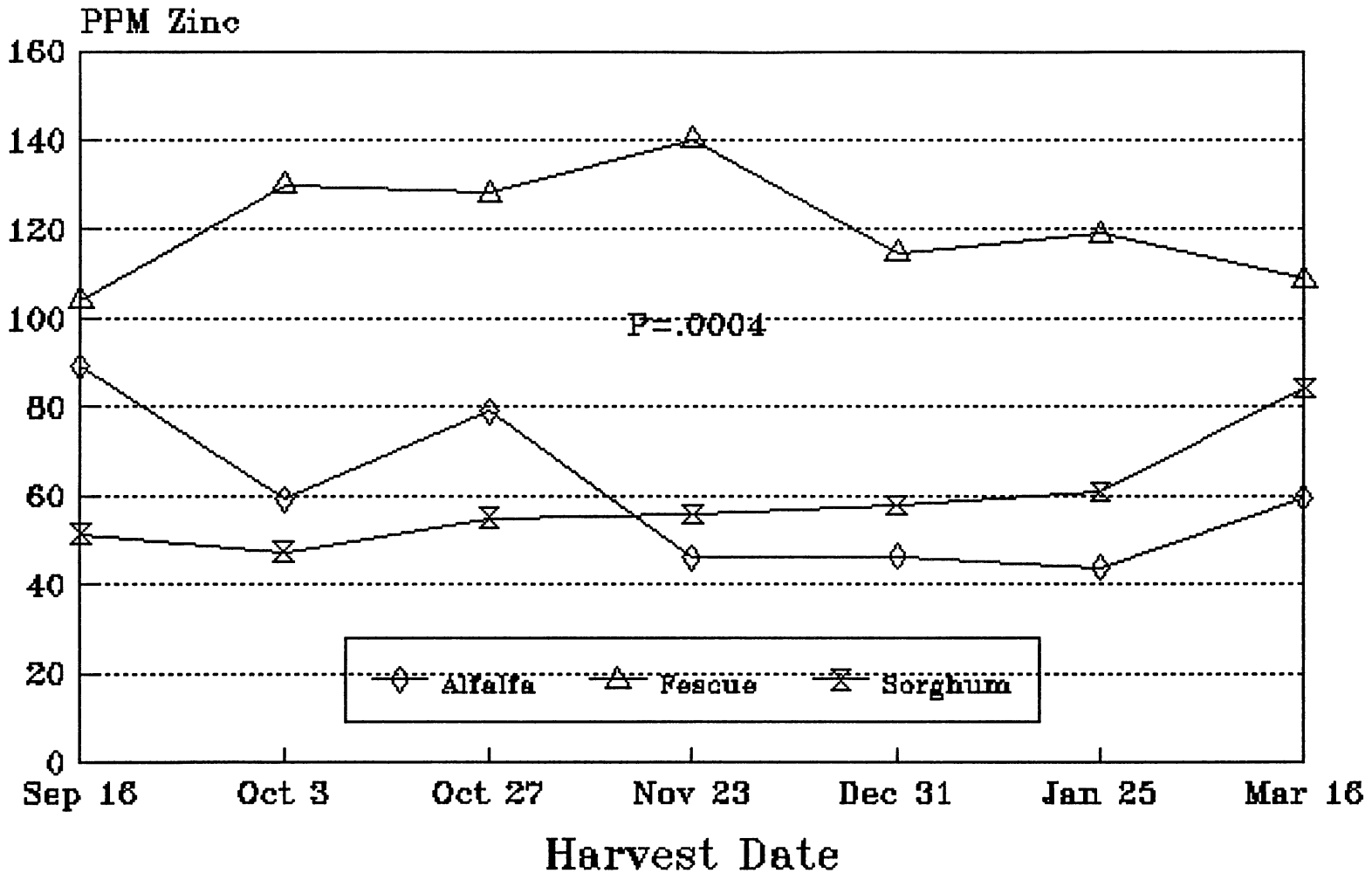

Figure 12. Average Zinc Concentration in Forage Crops During Greenhouse Study.

Plant Discussion

For copper and zinc to be available for plant uptake the proper ionic form must exist. The divalent zinc cation is the available form to plants. The mono and divalent copper cation is available to plant uptake. However, the divalent form is the most common for plant use. As stated earlier, there were higher than adequate levels of copper and zinc in plant dry tissue, 2 and 4.5 times respectively. These increased levels were due to the increased available forms of these metals in the sewage sludge. The addition of fly ash to increase the pH reduced the available copper and zinc by the formation of unavailable forms most likely a carbonate (Lindsay and Norvell, 1978).

There is no known requirement for nickel in plants. Copper and zinc are required for plant growth and uptake rates are linked to plant stress and growth stage. Since there is no known nickel requirment and, therefore, no selective mechanism for plant uptake. Nickel acculmulation is plants is likely to be dependent upon growth rate or rate of transpiration (root uptake of water). Nickel uptake could be more consistent than the other metals examined since there is no operative requirement as there is for copper and zinc. This may account for the uptake trend displayed in Figure 11.

Soils Results and Discussion

The analysis of the DTPA extract for available copper,

nickel and zinc revealed several pH interactions regrading the availability and mobility of the elements examined. Available copper showed no statistical evidence of being pH dependent with the pH range examined. The amount of available copper, as Figure 13 displays, increased during the greenhouse experiment for all pH ranges examined. However, the no treatment columns had the overall highest increase in DTPA available copper with an average increase of 0.80 ppm. Available copper increased slightly in the pH 6.8 and 7.0 fly ash treatments with 0.289 ppm and 0.294 ppm respectively. The probability coefficient for an available copper-pH interaction was a large 0.90.

Nickel availability after fly ash treatments responded much like zinc. However, mineralization of nickel from organic matter was not apparent, evidenced by an average 0.45 ppm nickel availability decrease during the greenhouse study. The columns treated with fly ash to pH 6.8 and 7.0, showed a much greater overall available nickel reduction, decreasing 1.19 ppm and 0.91 ppm respectively. Figure 14 displays a bar graph of available nickel in relation to pH. Soil zinc became less available with each fly ash addition to increase the pH. Figure 15 shows an overall increase of 4ppm zinc in the sludged soil maintained at pH 6.4 during the greenhouse study, likely due to organic matter oxidation and release of zinc.

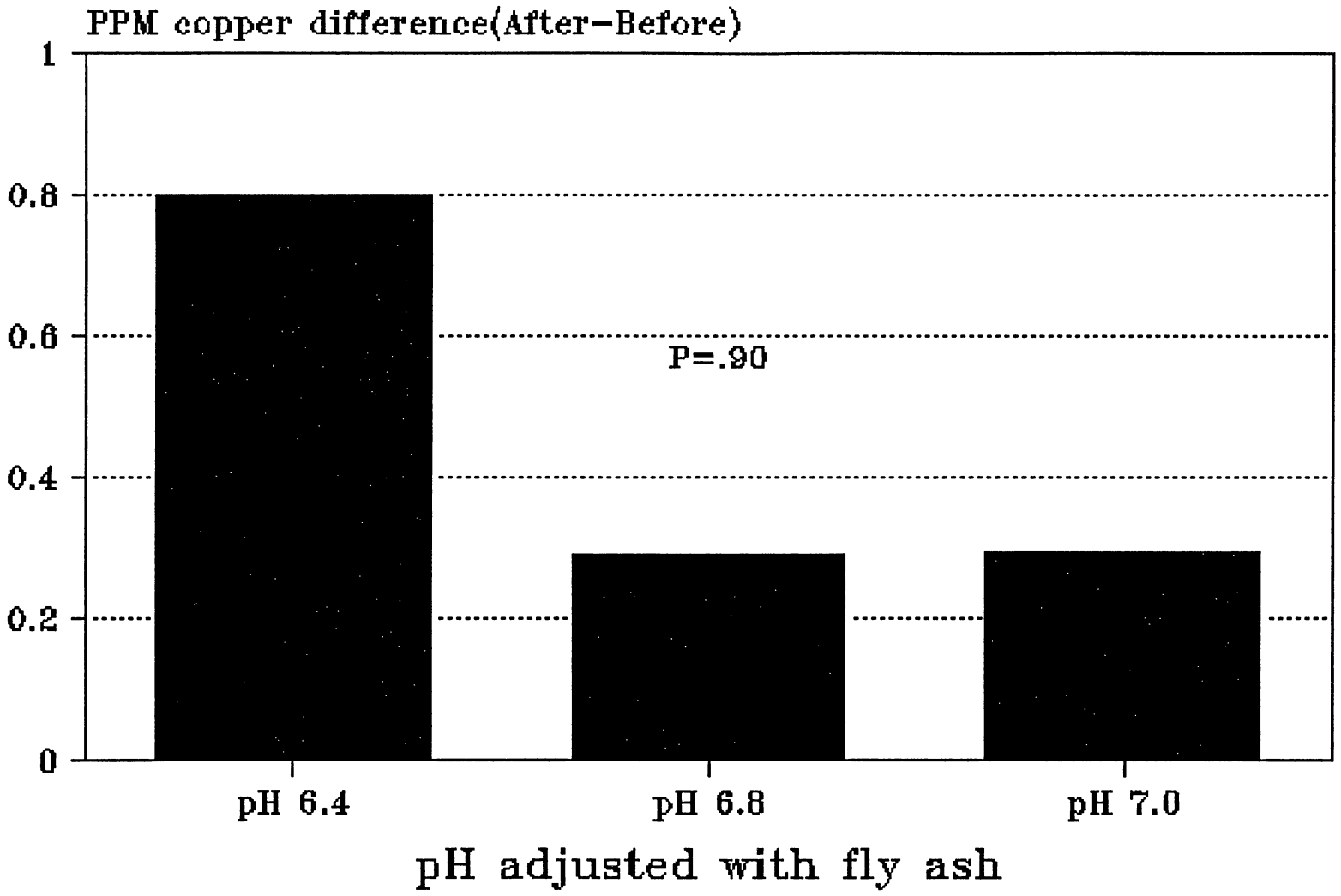

Figure 13. The Mean Difference of Copper Concentration in Soil Columns Due to the Addition of Fly Ash.

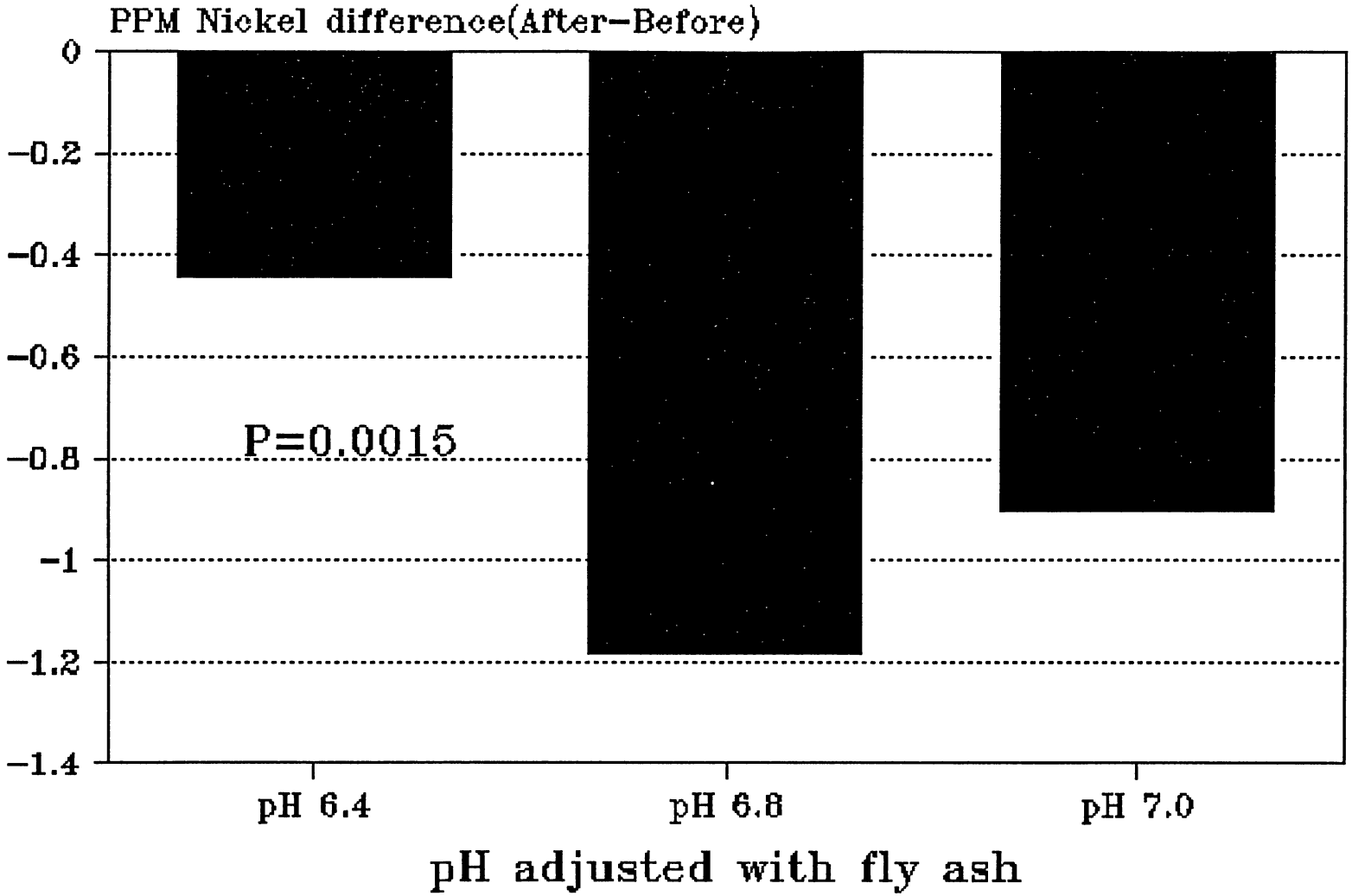

Figure 14. The Mean Difference of Nickel Concentration in Soil Columns Due to the Addition of Fly Ash.

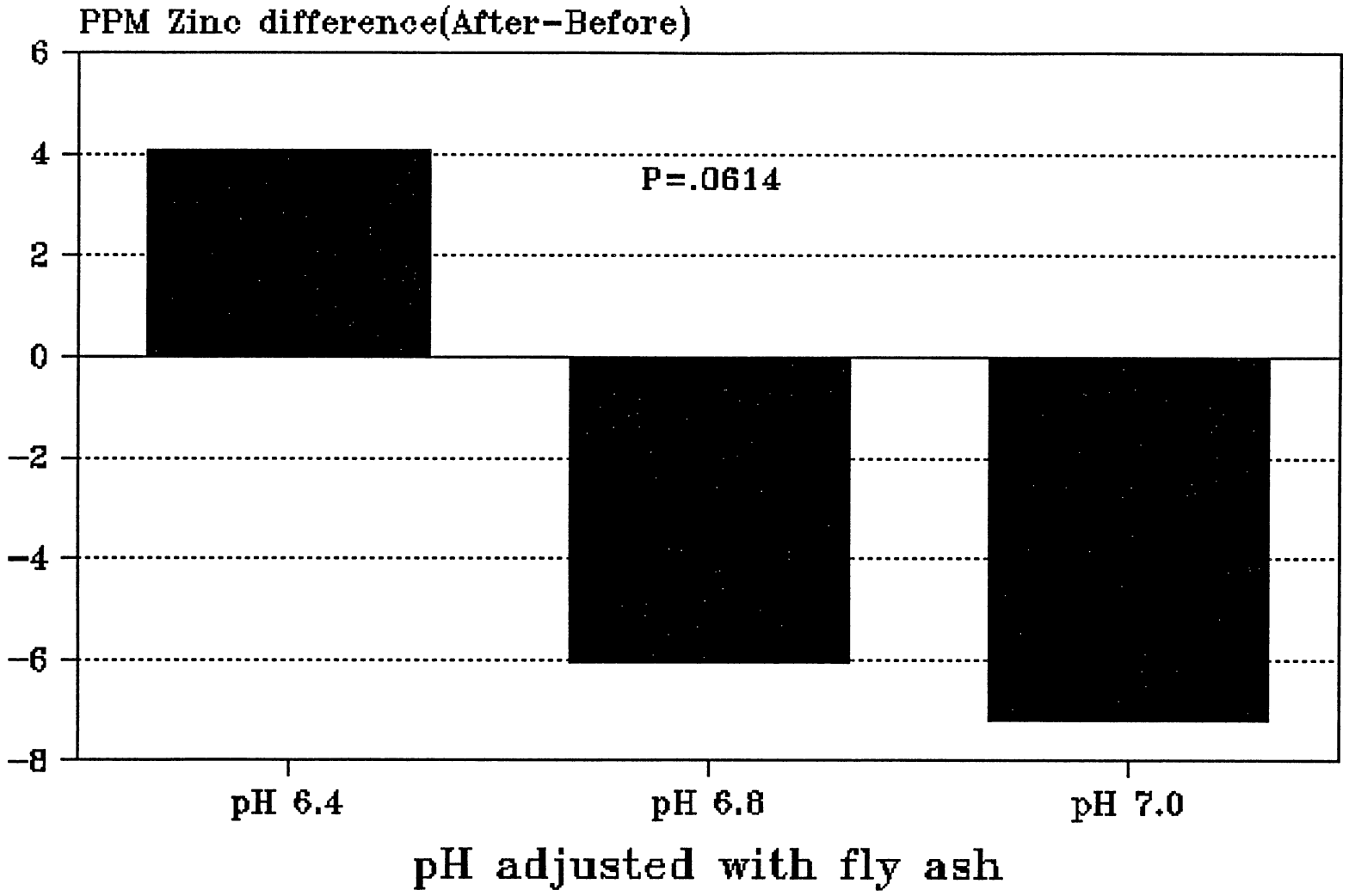

Figure 15. The Mean Difference of Zinc Concentration in Soil Columns Due to the Addition of Fly Ash.

While, the soil columns that received 14.8 Mg/ha equivalent of fly ash to adjust the pH to 6.8, had a decrease of 6.05 ppm of available zinc. Also, columns treated with 19.10 Mg/ha adjusting to pH 7.0, decreased the available zinc by 7.20 ppm. This pH-zinc availability relationship has a probability coefficient of 0.0614.

The examination of each of the five column zones for available copper, nickel and zinc permitted an evaluation of element mobility. Copper, as before, showed no statistical evidence of having a pH-zone interaction during the greenhouse experiment. This is illustrated with Figure 16. The upper horizons of the high fly ash treatment to pH 7.0 had an overall 0.92 ppm available copper increase. The lower fly ash treatment to pH 6.8, increased available copper 0.63 ppm. However, the no treatment columns had the largest increase of available copper with a 1.87 ppm increase during the greenhouse experiment. This increase is most likely attributed to mineralization of copper from sludge. Figure 17 details available nickel throughout the column profile. It can be observed that nickel availability decreased with the fly ash treatments. The addition of 14.8 Mg/ha decreased nickel availability in the upper horizon (zones 1 and 2) by an average of 2.95 ppm. The addition of 19.10 Mg/ha of fly ash decreased nickel availability in upper horizon by an average of 2.24 ppm. The uppermost subsoil zone (zone 3) had a slight overall increase in available nickel of 0.02 ppm. This average increase is not

significant but is attributed to slight nickel movement form the upper sludged profile.

It should be noted that the no treatment columns had a available nickel reduction in the upper horizon of 1.14 ppm, which is 61.36% less than pH 7.0 and 51.49% less than pH 6.8. Zinc, as represented by Figure 18, which displays a strong pH-zone interaction with a probability coefficient of 0.001. The highest fly ash treatment, adjusting the pH to 7.0, decreased available zinc in the sludge horizon by 17.54 ppm. The pH 6.8 replications had similar results with an average available zinc reduction of 14.71 ppm for the sludge horizon. In contrast, the no treatment columns had an average increase of 10.41 ppm of available zinc.

Available soil nickel vs. pH.

The different pH values of available soil nickel was statistically examined through the use of LSD's. The concentration of available soil nickel was found to be significantly higher at pH 6.4 when compared to pH 6.8. However, the concentrations of available soil nickel were found to be the same at pH 6.8 and pH 7.0.

The concentration of available soil copper showed no significant difference at any of the pH ranges examined when the LSD analysis was used.

The concentration of available soil zinc at the various pH values examined responded much like soil nickel, being statistically different at pH 6.4 when compared to 6.8 and being statistically alike at pH values of 6.8 and 7.0.

Based on the data presented, fly ash is shown to be effective for stabilization of heavy metals derived from sewage sludge.

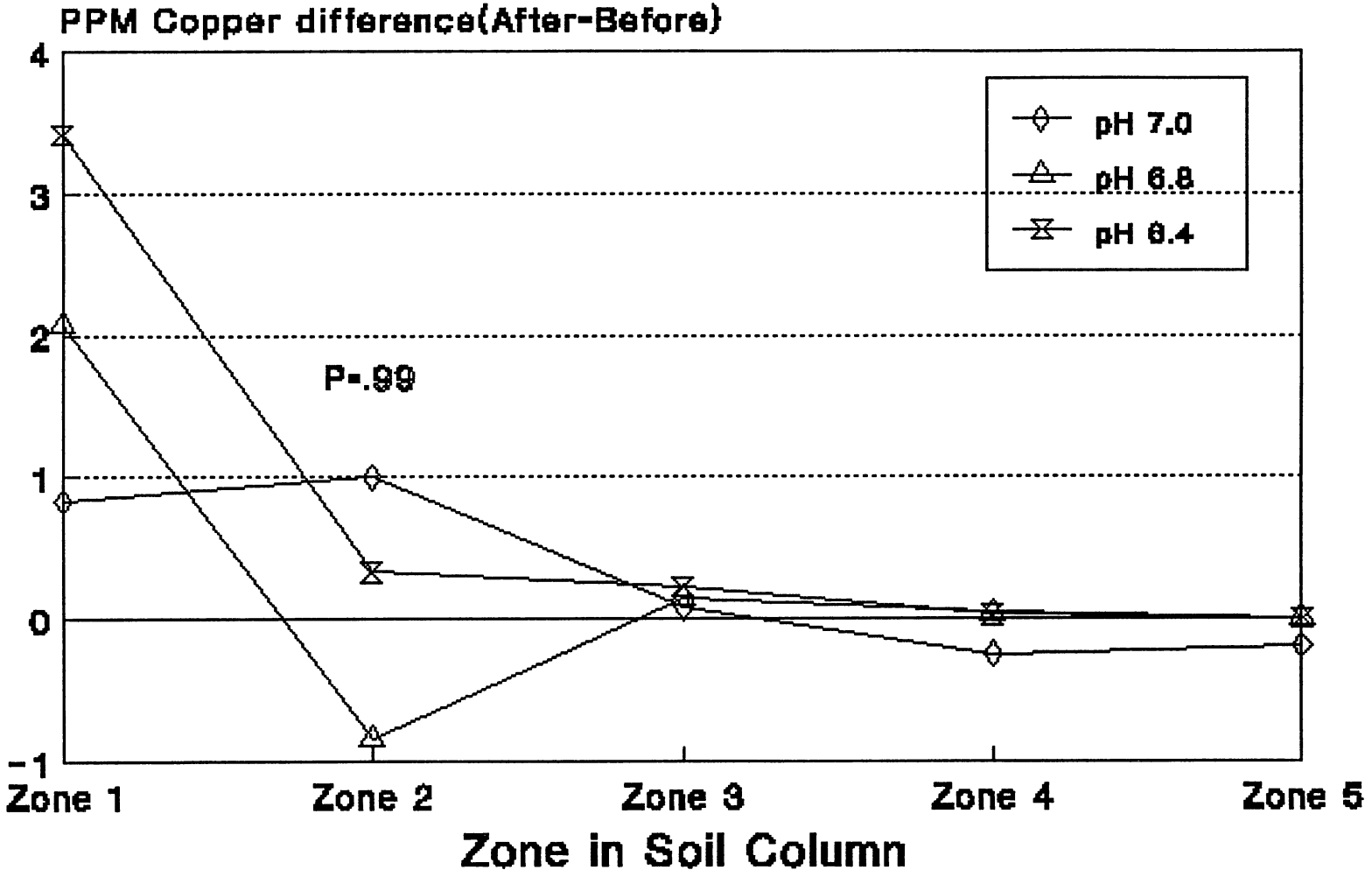

Figure 16. The Difference in Copper Concentrations Resulting From a pH Change Due to the Addtion of Fly Ash.

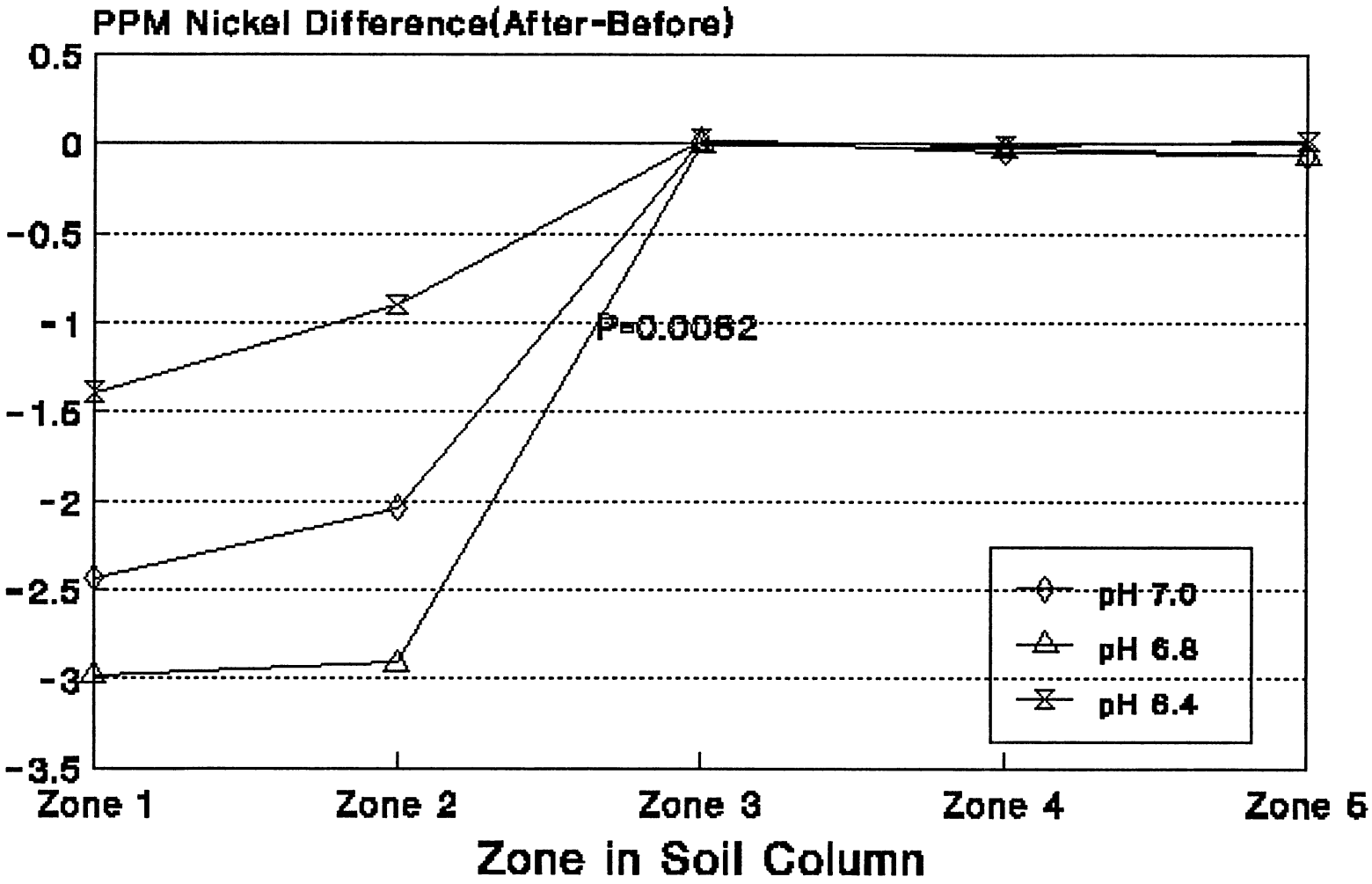

Figure 17. The Difference in Nickel Concentrations Resulting from a pH Change Due to Fly Ash Addition.

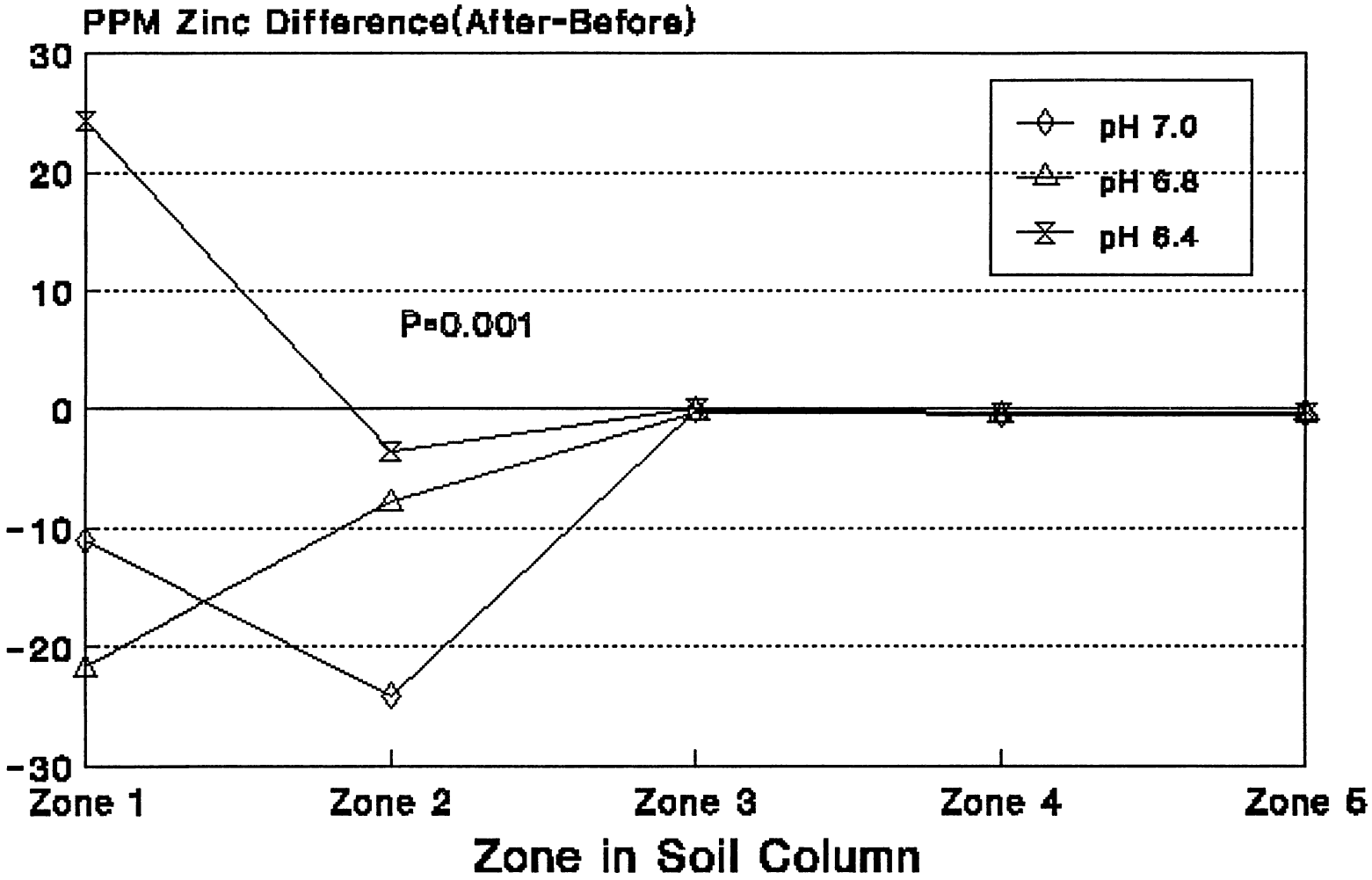

Figure 18. The Difference in Zinc Concentration Resulting from a pH Change Due to Fly Ash Addition.

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APPENDIXES

APPENDIX A

SAS GENERAL LINEAR MODELS PROCEDURE

FOR PLANT COPPER

METAL=C

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE MCONT

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C V
MODEL	179	2838 36110639	15 85676596	2 59	0 0001	0 876983	20 5476
ERROR	65	398 14501606	6 12530794		ROOT MSE		MCONT MEAN
CORRECTED TOTAL	244	3236 50612245			2 47493595		12 04489796

SOURCE	DF	TYPE I SS	F VALUE	PR > F
REP	3	75 80647009	4 13	0 0097
CROP	2	494 95220002	40 40	0 0001
PH	2	341 00578352	27 84	0 0001
CROP*PH	4	272 21646029	11 11	0 0001
REP*CROP*PH	24	200 83473234	1 37	0 1609
HDATE	6	273 43333333	7 44	0 0001
REP*HDATE	18	185 27334656	1 68	0 0664
CROP*HDATE	12	329 53628378	4 48	0 0001
REP*CROP*HDATE	36	273 41576649	1 24	0 2227
PH*HDATE	12	67 79271284	0 92	0 5304
REP*PH*HDATE	36	138 16826599	0 63	0 9350
CROP*PH*HDATE	24	185 92575113	1 26	0 2251

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*CROP*PH AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
CROP	2	494 95220002	29 57	0 0001
PH	2	341 00578352	20 38	0 0001
CROP*PH	4	272 21646029	8 13	0 0003

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*HDATE AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
HDATE	6	273 43333333	4 43	0 0064

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*CROP*HDATE AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
CROP*HDATE	12	329 53628378	3 62	0 0014

APPENDIX B

SAS GENERAL LINEAR MODELS PROCEDURE

FOR PLANT NICKEL

METAL=N

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE MCONT

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C V
MODEL	179	4318 55251323	24 12599169	3 85	0 0001	0 913781	15 5414
ERROR	65	407 47197657	6 26879964		ROOT MSE		MCONT MEAN
CORRECTED TOTAL	244	4726 02448980			2 50375710		16 11020408

SOURCE	DF	TYPE I SS	F VALUE	PR > F
REP	3	40 12355466	2 13	0 1045
CROP	2	132 97454882	10 61	0 0001
PH	2	1509 16623438	120 37	0 0001
CROP*PH	4	209 76156307	8 37	0 0001
REP*CROP*PH	24	104 66525554	0 70	0 8376
HDATE	6	211 64691877	5 63	0 0001
REP*HDATE	18	553 63218176	4 91	0 0001
CROP*HDATE	12	360 56114289	4 79	0 0001
REP*CROP*HDATE	36	726 69943912	3 22	0 0001
PH*HDATE	12	92 50039683	1 23	0 2828
REP*PH*HDATE	36	215 08161376	0 95	0 5534
CROP*PH*HDATE	24	161 73966364	1 08	0 3951

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*CROP*PH AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
CROP	2	132 97454882	15 25	0 0001
PH	2	1509 16623438	173 03	0 0001
CROP*PH	4	209 76156307	12 02	0 0001

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*HDATE AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
HDATE	6	211 64691877	1 15	0 3762

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*CROP*HDATE AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
CROP*HDATE	12	360 56114289	1 49	0 1739

APPENDIX C

SAS GENERAL LINEAR MODELS PROCEDURE

FOR PLANT ZINC

METAL=Z

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE MCONT

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C V
MODEL	179	415398 68802595	2320 66306160	5 35	0 0001	0 936384	25 8469
ERROR	65	28221 24666793	434 17302566		ROOT MSE		MCONT MEAN
CORRECTED TOTAL	244	443619 93469388			20 83681899		80 61632653

SOURCE	DF	TYPE I SS	F VALUE	PR > F
REP	3	9297 80814094	7 14	0 0003
CROP	2	206121 74797389	237 37	0 0001
PH	2	40497 30856843	46 64	0 0001
CROP*PH	4	31905 10073799	18 37	0 0001
REP*CROP*PH	24	15447 20736787	1 48	0 1069
HDATE	6	4835 32212885	1 86	0 1020
REP*HDATE	18	10457 29824152	1 34	0 1950
CROP*HDATE	12	38325 06514979	7 36	0 0001
REP*CROP*HDATE	36	27350 85416238	1 75	0 0248
PH*HDATE	12	3889 44963925	0 75	0 7012
REP*PH*HDATE	36	18924 67999038	1 21	0 2478
CROP*PH*HDATE	24	8346 84592467	0 80	0 7221

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*CROP*PH AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
CROP	2	206121 74797389	160 12	0 0001
PH	2	40497 30856843	31 46	0 0001
CROP*PH	4	31905 10073799	12 39	0 0001

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*HDATE AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
HDATE	6	4835 32212885	1 39	0 2728

TESTS OF HYPOTHESES USING THE TYPE I MS FOR REP*CROP*HDATE AS AN ERROR TERM

SOURCE	DF	TYPE I SS	F VALUE	PR > F
CROP*HDATE	12	38325 06514979	4 20	0 0004

APPENDIX D

SAS ANALYSIS OF VARIANCE PROCEDURE

FOR SOIL COPPER

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE C

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C V
MODEL	71	3866 68667278	54 46037567	1 16	0 2389	0 433016	1483 9645
ERROR	108	5062 96648000	46 87931926		ROOT MSE		C MEAN
CORRECTED TOTAL	179	8929 65315278			6 84684740		0 46138889

SOURCE	DF	ANOVA SS	F VALUE	PR > F
REP	3	1001 09749944	7 12	0 0002
CROP	2	0 94084111	0 01	0 9900
PH	2	10 33018778	0 11	0 8958
CROP*PH	4	412 08225889	2 20	0 0740
REP*CROP*PH	24	1206 20844556	1 07	0 3872
ZONE	4	124 19067778	0 66	0 6195
CROP*ZONE	8	41 15649222	0 11	0 9988
PH*ZONE	8	51 45414556	0 14	0 9974
CROP*PH*ZONE	16	1019 22612444	1 36	0 1764

TESTS OF HYPOTHESES USING THE ANOVA MS FOR REP*CROP*PH AS AN ERROR TERM

SOURCE	DF	ANOVA SS	F VALUE	PR > F
CROP	2	0 94084111	0 01	0 9907
PH	2	10 33018778	0 10	0 9027
CROP*PH	4	412 08225889	2 05	0 1192

APPENDIX E

SAS ANALYSIS OF VARIANCE PROCEDURE

FOR SOIL NICKEL

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE N

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C V
MODEL	71	318 30884778	4 48322321	4 26	0 0001	0 736917	120 3797
ERROR	108	113 63775000	1 05220139		ROOT MSE		N MEAN
CORRECTED TOTAL	179	431 94659778			1 02576868		-0 85211111

SOURCE	DF	ANOVA SS	F VALUE	PR > F
REP	3	26 14411333	8 28	0 0001
CROP	2	2 32208444	1 10	0 3354
PH	2	16 88844444	8 03	0 0006
CROP*PH	4	9 05356889	2 15	0 0794
REP*CROP*PH	24	23 58978667	0 93	0 5568
ZONE	4	190 86503667	45 35	0 0001
CROP*ZONE	8	6 23706000	0 74	0 6552
PH*ZONE	8	23 20716667	2 76	0 0082
CROP*PH*ZONE	16	20 00158667	1 19	0 2892

TESTS OF HYPOTHESES USING THE ANOVA MS FOR REP*CROP*PH AS AN ERROR TERM

SOURCE	DF	ANOVA SS	F VALUE	PR > F
CROP	2	2 32208444	1 18	0 3241
PH	2	16 88844444	8 59	0 0015
CROP*PH	4	9 05356889	2 30	0 0878

APPENDIX F

SAS ANALYSIS OF VARIANCE PROCEDURE

FOR SOIL ZINC

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: Z

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C V
MODEL	71	48373 24005278	681 31324018	1 61	0 0129	0 513730	670 5598
ERROR	108	45787 65038000	423 95972574		ROOT MSE		Z MEAN
CORRECTED TOTAL	179	94160 89043278			20 59028231		-3 07061111

SOURCE	DF	ANOVA SS	F VALUE	PR > F
REP	3	2194 52521056	1 73	0 1661
CROP	2	722 10816778	0 85	0 4296
PH	2	4599 46721444	5 42	0 0057
CROP*PH	4	1200 27208556	0 71	0 5883
REP*CROP*PH	24	17564 24783444	1 73	0 0310
ZONE	4	3583 64483556	2 11	0 0841
CROP*ZONE	8	1496 08418778	0 44	0 8939
PH*ZONE	8	12148 39730778	3 58	0 0010
CROP*PH*ZONE	16	4864 49320889	0 72	0 7713

TESTS OF HYPOTHESES USING THE ANOVA MS FOR REP*CROP*PH AS AN ERROR TERM

SOURCE	DF	ANOVA SS	F VALUE	PR > F
CROP	2	722 10816778	0 49	0 6166
PH	2	4599 46721444	3 14	0 0614
CROP*PH	4	1200 27208556	0 41	0 7996

VITA

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